

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
21 February 2002 (21.02.2002)

PCT

(10) International Publication Number  
**WO 02/15302 A2**

(51) International Patent Classification<sup>2</sup>: **H01M 4/00**

(21) International Application Number: **PCT/US01/41713**

(22) International Filing Date: 14 August 2001 (14.08.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/225,158 14 August 2000 (14.08.2000) US  
60/264,150 25 January 2001 (25.01.2001) US

(71) Applicant: **WORLD PROPERTIES INC.** [US/US];  
Suite 410, 7366 North Lincoln Avenue, Lincolnwood, IL  
60646 (US).

(72) Inventors: **FITTS, Bruce, B.**; 86 Jacques Road, Danielson, CT 06239 (US). **LANDI, Vincent, R.**; 240 Green Hollow Road, Danielson, CT 06239 (US). **ROY, Saroj, K.**; 840 North Main Street, Danielson, CT 06239 (US).

(74) Agent: **REIMER, Leah, M.**; Cantor Colburn LLP, 55 Griffin Road South, Bloomfield, CT 06002 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



**WO 02/15302 A2**

(54) Title: **THERMOSETTING COMPOSITION FOR ELECTROCHEMICAL CELL COMPONENTS AND METHODS OF MAKING THEREOF**

(57) Abstract: A conductive, moldable composite material for the manufacture of electrochemical cell components comprising a thermosetting resin system and conductive filler wherein the thermosetting resin composition comprises: (1) a polybutadiene or polyisoprene resin; (2) an optional functionalized liquid polybutadiene or polyisoprene resin; (3) an optional butadiene- or isoprene-containing copolymer; and (4) an optional low molecular weight polymer. In a preferred embodiment, the conductive moldable composite material is used to form a bipolar plate, current collector or other electrochemical cell component. Articles made of the conductive moldable composite material are resistant to chemical attack and hydrolysis, have excellent mechanical strength and toughness, have a volume resistivity of about 1.006 ohm-cm or less and preferably about 0.04 ohm-cm or less and a thermal conductivity of at least about 5 watts/meter °K.

**THERMOSETTING COMPOSITION FOR ELECTROCHEMICAL CELL  
COMPONENTS AND METHODS OF MAKING THEREOF**

**BACKGROUND OF THE INVENTION**

This invention relates to conductive materials, and in particular to conductive thermosetting compositions which find particular utility in the manufacture of electrochemical cell components, and methods of making thereof.

Conductive, moldable composite materials are actively being sought for use in 5 electrochemical cells, which includes both electrolysis cells and fuel cells. A preferred type of electrochemical cell is the "proton exchange membrane" cell, wherein the cathode of the cell is separated from the anode by a proton exchange membrane that facilitates the diffusion of ions and/or water between the cathode and anode.

10 The typical electrochemical cell includes a number of individual cells arranged in a stack, with the working fluid directed through the cells via input and output conduits formed within the stack structure. The cells within the stack are sequentially arranged, each including a cathode, a proton exchange membrane, and an anode.

15 Membrane electrode assemblies ("MEAs") for use in fuel cells are well known, being described for example in U.S. Patent Nos. 5,272,017 and 3,134,697, which are incorporated by reference herein. The MEA for each cell is placed between a pair of electrically conductive elements which serve as current collectors for the anode/cathode, and which generally contain an array of grooves in the faces thereof for distributing the gaseous reactants ( $H_2$  and  $O_2/air$ ) over the surfaces of the anode 20 and cathode. The gaseous  $O_2/air$  reactant is usually saturated, typically with water.

25 Electrochemical cell systems generally comprise a plurality of such cells, which are stacked together in electrical series separated from each other by an impermeable, electrically conductive plate referred to as a bipolar plate. The bipolar plate thus serves as an electrically conductive separator element between two adjacent cells, and generally also has reactant gas distributing grooves on both external faces thereof. In most cases the bipolar plate also has internal passages through which coolant flows to remove heat from the stack. In the electrochemical cell environment,

the exterior faces of the bipolar plates are in constant contact with often highly corrosive, acidic solutions at elevated temperatures. Moreover, at least one of the electrode faces may be polarized in the presence of pressurized, saturated air or hydrogen. To survive in such an environment, the bipolar plates must be able to 5 withstand these pressures and be highly resistant to corrosion and degradation.

Bipolar plates are often fabricated from graphite, which is lightweight, corrosion resistant, and electrically conductive. However, graphite is quite brittle and thus prone to cracking, and mechanically difficult to handle, thus increasing production costs. Additionally, graphite is porous, making it virtually impossible to 10 make the very thin, gas-impervious plates that are desirable for low-weight, low-volume electrochemical cell stacks. The graphite plates must also be operably connected to the other components by seal rings. Typically the seal ring material contains plasticizers and additives that leach out over time and contaminate the catalyst, which generally halts energy production.

15 PCT Application 99/19389 to Choate et al., U.S. Patent No. 6,248,467 to Wilson et al., and U.S. Patent No. 6,251,308 to Butler disclose molding compositions with conductive fillers that can be formed into structures exhibiting electrical and thermal conductivity such as bipolar plates. The molding compositions typically employ a low viscosity resin system, specifically epoxy, epoxy vinyl ester, and 20 phenolic resin systems. While these compositions may offer some improvements to electrochemical cell technology, they may not have sufficient long-term chemical resistance. Materials employed in the electrochemical cell must be resistant to degradation in a particularly punishing environment over periods of time measured in years.

25 Accordingly, there is a perceived need in the art for a low cost, conductive molding composition with a high chemical resistance for use in electrochemical cells and methods of making thereof.

#### BRIEF SUMMARY OF THE INVENTION

30 The above described drawbacks and deficiencies are overcome by a conductive, moldable composite material for the manufacture of electrochemical cell

components, comprising a thermosetting resin system and conductive filler, wherein the thermosetting resin composition comprises: (1) a polybutadiene or polyisoprene resin; (2) an optional, functionalized liquid polybutadiene or polyisoprene resin; (3) an optional butadiene- or isoprene-containing copolymer; and (4) an optional low molecular weight polymer. In a preferred embodiment, the conductive moldable composite material is used to form a bipolar plate, current collector or other electrochemical cell component. In another embodiment, articles made of the conductive, moldable composite material are resistant to chemical attack and hydrolysis, have excellent mechanical strength and toughness, have a volume resistivity of about 0.116 ohm-cm or less, and have a thermal conductivity of at least about 5 watts/meter °K (W/m°K). Articles have a linear shrinkage per unit length of the molded composite in the X-Y plane less than or equal to about 0.005, measured as described in ASTM D-955. In addition, the conductive, moldable composite material as well as articles made from it are economical to produce due to the inexpensive starting materials as well as the use of conventional processing equipment.

The above discussed and other features and advantages of the present invention will be appreciated and understood by those skilled in the art from the following detailed description.

## 20 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

A conductive, moldable composite material for the manufacture of electrochemical cell components comprises a thermosetting resin system and conductive filler wherein the thermosetting resin composition comprises: (1) a polybutadiene or polyisoprene resin; (2) an optional, functionalized liquid polybutadiene or polyisoprene resin; (3) an optional butadiene- or isoprene-containing polymer; and (4) an optional, low molecular weight polymer. In a preferred embodiment, the conductive moldable composite material is used to form a bipolar plate, current collector or other electrochemical cell component.

The resin system used to form the conductive, moldable composite material is a thermosetting composition generally comprising a polybutadiene resin, polyisoprene resin or mixture thereof. The polybutadiene or polyisoprene resins may be liquid or

solid at room temperature. Liquid resins may have a molecular weight greater than 5,000, but preferably have a molecular weight of less than 5,000 (most preferably between 1,000 and 3,000). The preferably liquid (at room temperature) resin portion maintains the viscosity of the composition at a manageable level during processing to 5 facilitate handling, and it also crosslinks during cure. Polybutadiene and polyisoprene resins having at least 90% 1,2-addition by weight are preferred because they exhibit the greatest crosslink density upon cure owing to the large number of pendant vinyl groups available for crosslinking. High crosslink densities are desirable because the products exhibit superior performance in an electrochemical cell environment at 10 elevated temperatures. A preferred resin is B3000 resin, a low molecular weight polybutadiene liquid resin having greater than 90 weight percent (wt.%) 1,2-addition. B3000 resin is commercially available from Nippon Soda Co., Ltd.

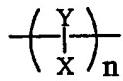
The resin system used to form the conductive, moldable composite optionally comprises functionalized liquid polybutadiene or polyisoprene resins. Examples of 15 appropriate functionalities for butadiene liquid resins include but are not limited to epoxy, maleate, hydroxy, carboxyl and methacrylate. Examples of useful liquid butadiene copolymers are butadiene-co-styrene and butadiene-co-acrylonitrile. Possible functionalized liquid polybutadiene resins include Nisso G-1000, G-2000, G-3000; Nisso C-1000; Nisso BN-1010, BN-2010, BN-3010, CN-1010; Nisso TE-2000; 20 and Nisso BF-1000 commercially available from Nippon Soda Co., Ltd. and Ricon 131/MA commercially available from Colorado Chemical Specialties, Inc.

The optional, butadiene- or isoprene-containing polymer is preferably 25 unsaturated and can be liquid or solid. It is preferably a solid, thermoplastic elastomer comprising a linear or graft-type block copolymer having a polybutadiene or polyisoprene block, and a thermoplastic block that preferably is styrene or  $\alpha$ -methyl styrene. Possible block copolymers, e.g., styrene-butadiene-styrene tri-block copolymers, include Vector 8508M (commercially available from Dexco Polymers, Houston, TX), Sol-T-6302 (commercially available from Enichem Elastomers American, Houston, TX), and Finaprene 401 (commercially available from Fina Oil 30 and Chemical Company, Dallas, TX). Preferably, the copolymer is a styrene-butadiene di-block copolymer, such as Kraton D1118X (commercially available from

Shell Chemical Corporation). Kraton D1118X is a di-block styrene-butadiene copolymer containing 30 vol% styrene.

The butadiene- or isoprene-containing polymer may also contain a second block copolymer similar to the first except that the polybutadiene or polyisoprene 5 block is hydrogenated, thereby forming a polyethylene block (in the case of polybutadiene) or an ethylene-propylene copolymer (in the case of polyisoprene). When used in conjunction with the first copolymer, materials with enhanced 10 toughness can be produced. Where it is desired to use this second block copolymer, a preferred material is Kraton GX1855 (commercially available from Shell Chemical Corp.), which is believed to be a mixture of styrene-high 1,2 butadiene-styrene block copolymer and styrene-(ethylene-propylene)-styrene block copolymer.

Thus, in a preferred embodiment, the butadiene- or isoprene-containing polymer comprises a solid thermoplastic elastomer block copolymer having the



formula  $X_m(Y-X)_n$  (linear copolymer) or (graft copolymer), where Y is a 15 polybutadiene or polyisoprene block, X is a thermoplastic block, and m and n represent the average block numbers in the copolymer, m is 0 or 1 and n is at least 1. The composition may further include a second thermoplastic elastomer block



copolymer having the formula  $W_p(Z-W)_q$  (linear copolymer) or (graft 20 copolymer) where Z is a polyethylene or ethylene-propylene copolymer block, W is a thermoplastic block, and p and q represent the average block numbers in the copolymer, p being 0 and 1 and q being at least 1.

The volume to volume ratio of the polybutadiene or polyisoprene resin to butadiene- or isoprene-containing polymer preferably is between 1:9 and 9:1, inclusive. The selection of the butadiene- or isoprene-containing polymer depends on 25 chemical and hydrolysis resistance as well as the toughness conferred upon the molded material.

The optional low molecular weight polymer resin is generally employed to enhance toughness and other desired characteristics of composition. Examples of suitable low molecular weight polymer resins include, but are not limited to, telechelic

polymers such as polystyrene, multifunctional acrylate monomers and ethylene propylene diene monomer (EPDM) containing varying amounts of pendant norbornene groups and/or unsaturated functional groups. The optional low molecular weight polymer resin can be present in amounts of about 0 to about 30 wt% of the  
5 resin composition.

Monomers with vinyl unsaturation, sometimes known as crosslinking agents, may also be included in the resin system for specific property or processing conditions, such as to decrease the viscosity of the conductive moldable composite material, especially with high filler loading. Viscosity is a key factor in obtaining  
10 acceptable molding rheologies. Inclusion of one or more monomers with vinyl unsaturation has the added benefit of increasing crosslink density upon cure. Suitable monomers must be capable of co-reacting with one of the other resin system components. Examples of suitable monomers include styrene, vinyl toluene, divinyl benzene, triallylcyanurate, diallylphthalate, and multifunctional acrylate monomers  
15 (such as Sartomer compounds available from Arco Specialty Chemicals Co.), among others, all of which are commercially available. The useful amount of monomers with vinyl unsaturation is about 0% by weight to about 80% by weight of the resin composition and preferably about 3% to about 50%.

A curing agent is preferably added to the resin system to accelerate the curing  
20 reaction. When the composition is heated, the curing agent decomposes to form free radicals, which then initiate cross linking of the polymeric chains. Preferred curing agents are organic peroxides such as Luperox, dicumyl peroxide, t-butyl perbenzoate, 2,5-dimethyl-2,5-di(t-butyl peroxy)hexane,  $\alpha,\alpha'$ -bis(t-butyl peroxy)diisopropylbenzene, and 2,5-dimethyl-2,5-di(t-butyl peroxy) hexyne-3, all of  
25 which are commercially available. They may be used alone or in combination. Typical amounts of curing agent are from about 1.5 part per hundred parts of the total resin composition (PHR) to about 6 PHR.

Useful conductive fillers include metal fillers that do not leach, thus poisoning  
the catalyst, for example pure nickel (Ni), or 316 stainless steel. Carbonaceous  
30 conductive fillers are preferred due to their resistance to acid environments. Examples of carbonaceous fillers are carbon fibers, coke, natural and synthetic graphite powder,

vapor grown carbon fibers, carbon nanotubes, carbon microtubes, carbon black, and chemically modified, e.g., coated carbon black with enhanced electrical properties. These fillers may be used alone or in combination. Combinations of filler may be desirable to maximize the packing density of the filler and thereby maximize the  
5 electrical conductivity of the molded composite.

Useful amounts of filler are about 10% to about 90% by volume of the total conductive molding composite material. Alternately useful amounts of filler are about 19.5 weight percent (wt%) to about 95.0 weight percent (wt%), preferably about 50 to about 95 wt%; more preferably about 80 to about 95 wt% based on the total weight of  
10 the conductive molding composite material.

The fillers may have varying particle shapes, sizes and purities. Preferably some or all of the filler is in the form of fibers, microtubes, single wall or multi-wall graphite, single wall or multi-wall carbon nanotubes, platelets, or combinations comprising at least one of the foregoing filler forms. Fibers are herein defined as  
15 particles having a length to diameter ratio of at least about 2, preferably at least about 5 and more preferably at least about 100. Fibers having a length to diameter ratio of at least about 400 to about 10,000, which are known as high aspect ratio fillers, are preferred. Nanotubes and microtubes are exemplary high aspect ratio fillers. Platelets are herein defined as particles having two dimensions which are greater than a third  
20 dimension by at least a factor of two, preferably by greater than a factor of five. For example, the width and length are each at least two times greater than the height, or the diameter of a disk-shaped particle is at least two times greater than the height. Platelets may have regular or irregular geometries. Use of filler comprising fiber and/or platelets helps to decrease the amount of shrinkage of the composite material  
25 during cure. Particles wherein the longest single linear dimension is about 0.2 to 6000 micrometers may be used.

The conductive moldable composite material may further include various other additives for improving thermal conductivity, impact properties, mold-release properties, and thermo-oxidative stability. These additives are generally non-  
30 electrically conductive. Thermal conductivity can be improved with the addition of metal oxides, nitrides, carbonates or carbides (hereinafter sometimes referred to as

"ceramic additives"). Such additives can be in the form of powders, flakes or fibers. Exemplary materials include oxides, carbides, carbonates, and nitrides of tin, zinc, copper, molybdenum, calcium, titanium, zirconium, boron, silicon, yttrium, aluminum or magnesium; mica; glass ceramic materials; or fused silica. When present, the 5 thermally conducting materials are preferably present between about 60 to about 200 parts of thermally conducting material per 100 parts of total resin ("PHR"), and more preferably about 80 to about 180 PHR. The amounts of the above additives should not impair molding operations.

In general, the conductive molding composite material is processed as follows. 10 First, all the components (the resin system, curing agent, filler and a volatile solvent when used) are thoroughly mixed in conventional mixing equipment. The mixing temperature is regulated to avoid substantial decomposition of the curing agent (and thus premature cure). Additionally, a small amount of an inhibitor, about 50 to about 350 parts per million by weight of resin, may be added to protect against peroxide 15 decomposition. Mixing continues until the filler is uniformly dispersed through the resin. Additional solvent may be added to facilitate the formation of small particles.

The homogenized mixture is then removed, cooled and dried. If necessary the material may be deagglomerated by passing it through a coarse screen. Next, the particles are poured, pressed or injected into a mold, such as a compression, injection 20 or transfer mold. Compression molding is preferred when some or all of the filler is in the form of fibers and/or platelets. Without being bound by theory, it is believed that the filler particles can become oriented during compression molding which reduces shrinkage of the composite material during cure. Alternatively, an extruder is used and the material is molded into the desired shape. The shaped article is cured in 25 either a one or two step cure process.

In the two step cure process, the first step is a conventional peroxide cure step; typical cure temperatures are between about 150°C and about 200°C. If the method used to form the conductive moldable composite material into the desired shape heats the article to a temperature between about 150°C and about 200°C, then the forming 30 step also constitutes the first cure step. Compression molding is one method of forming an article from the conductive moldable composite material which also

functions as the first cure step. The second step of the cure process can either be a high temperature cure or high-energy electron beam irradiation cure (E-beam cure). A high temperature cure comprises heating the article to temperatures greater than about 230°C but less than the decomposition temperature of the material, generally about 5 400°C under an inert atmosphere.

E-beam curing is advantageous because it allows for controlled curing for a given system. The amount of curing (cross linking) is controlled by the total amount of radiation given to the article. The ability of the high-energy electrons to penetrate through the sample to specific depth is known as the penetration depth. The 10 penetration depth is controlled by the E-beam source, and different sources give different penetration depths. The combined flexibility in the amount of curing as well as the depth of curing allows the production of articles with a range of physical dimensions, in particular thickness, as well as physical properties from the same conductive moldable composite material.

15 Articles made of the conductive moldable composite material are resistant to chemical attack and hydrolysis, and have excellent mechanical strength and toughness. The articles preferably have a volume resistivity of about 0.116 ohm-cm or less, preferably about 0.08 ohm-cm or less and most preferably about 0.045 ohm-cm or less.

20 The articles further possess a thermal conductivity of at least about 5 watts/meter °K, preferably at least about 7 watts/meter °K and more preferably at least about 9 watts/meter °K.

The linear shrinkage per unit length of the molded composite in the X-Y plane 25 is less than or equal to about 0.005, preferably less than or equal to about 0.003, and most preferably less than or equal to about 0.001. Linear shrinkage per unit length of the molded composite is defined by ASTM D-955. Generally speaking it is the amount of shrinkage either in length (Y-direction) or width (X-direction) versus the corresponding original part dimension.

The method of the invention is further illustrated by the following examples 30 which are meant to be illustrative, not limiting.

-10-

## EXAMPLES

### Examples 1-8

The conductive moldable composite materials of the following examples were made using the formulation and components in Table 1 with the type of graphite varied by example. The resulting properties and graphite types are shown in Table 2.

Table 1

Component	Source, Trade Name	Vol. %
Liquid polybutadiene resin	Nisso B-3000	28.04
Trimethylolpropane trimethacrylate	Sartomer SR-350	0.91
t-Butyl perbenzoate	Triganox-C	0.23
Peroxide	Luprox 5OOR or Perkadox BC	2.36
Di-t-butyl-p-cresol	Ionol	0.15
Zinc stearate	-	1.54
Carbon fibers	Tenneco Avcarb 99 Type 401	14.60
Synthetic graphite	Varied by example	52.28

A dilute resin solution comprising up to about 50 parts by weight resin composition, preferably up to about 25 parts by weight resin composition and more preferably up to about 10 parts by weight resin composition and a volatile solvent, preferably acetone, was slowly added to the monomer, peroxides and inhibitor in a 10 Ross double planetary mixer and mixed to produce a homogeneous solution. (Other volatile solvents may also be used.) Zinc stearate, a mold release agent, was then added and thoroughly mixed into the solution. The solution was added incrementally to the carbon fibers and graphite and mixed until all filler was completely dispersed. Another 100 parts by weight of acetone was added and the mixture was mixed for 15 minutes. The resulting particulate material was removed from the mixer and spread on screens and allowed to dry at room temperature. Residual solvent was removed in a drying oven at 120°C. The material was then passed through a coarse screen.

The material was molded into disks about 2 inches (50 mm) in diameter with a thickness of about 0.125 inch (3.18 mm) by compression molding at 180°C for four 20 minutes. The disks were further cured in an oven at 240°C. The disks were tested for resistivity according to IPC-TM-650, flex stress and flex modulus according to ASTM

D-790-99, and thermal conductivity according to ASTM C-518. Values for flex stress are given in pounds per square inch (psi) and megapascals (MPa). Values for flex modulus are given in kilopounds per square inch (Kpsi) and megapascals (MPa).

Table 2

Ex.	Graphite Type	Flex Stress (psi/Mpa)	Flex Modulus (Kpsi/Mpa)	Thermal Conductivity (W/m°K)	Volume Resistivity (ohm-cm) at 0.125 inch
1	Asbury APS	2488/17.1	1316/9073	7	0.152
2	Asbury 4012	2515/17.3	781/5384	6	0.100
3	Asbury A99	3821/26.3	970/6687	16	0.0253
4	Asbury A60	2325/16.0	830/5722	7	0.057
5	Asbury A230U	2970/20.5	902/6219	14	0.025
6	Asbury 4957	1418/9.8	370/2551	17	0.0213
7	Asbury 3610	1717/11.8	567/3909	9	0.0441
8	Asbury 3621	1231/8.5	296/2040	12	0.0363

5           Example 1, when further comprising NZ33, a neoalkoxy zirconate produced by Kenrich Petrochemicals, Inc., as a coupling agent, has a maximum stress of 2366 psi (16.3 Mpa) and a flex modulus of 1140 Kpsi (7862 Mpa).

Examples 1–8 employ various kinds of graphites. These graphites can be differentiated primarily on the basis of their origin, carbon content, particle size, and 10 purity. Asbury APS is a synthetic graphite with a minimum carbon content of 95% and mean particle size of 35 micrometers. Asbury 4012 is a synthetic graphite with a minimum carbon content of 98% and a mean particle size of 140 micrometers, and Asbury A60 is a synthetic graphite with a minimum carbon content of 98% and a mean particle size of 65 micrometers. Asbury A99 is a synthetic graphite with a 15 minimum carbon content of 98% and a mean particle size of 25 micrometers, and Asbury A230U is a natural graphite with a very high carbon content and a mean particle size of 20 micrometers. Asbury 4957 is a hybrid graphite with a minimum carbon content of 99% and a mean particle size of 44 micrometers. Asbury 3610 is a natural flake graphite with a minimum carbon content of 99.5% and a mean particle

-12-

size of 75 micrometers. Asbury 3621 is also a natural graphite plate with minimum carbon content of 99.4% and a mean particle size of 300 micrometers.

#### Examples 9-14

- 5        The conductive moldable composite materials of the following examples were made using the formulation and components in Table 3 with the type of filler varied by example. The filler types and resulting properties are shown in Table 4 and Table 5.

Table 3

Component	Source, Trade Name	Vol. %
Liquid polybutadiene resin	Nisso B-3000	28.04
Trimethylolpropane trimethacrylate	Sartomer SR-350	0.91
t-butyl perbenzoate	Triganox-C	0.23
Peroxide	Luprox 5OOR or Perkadox BC	2.36
di-t-butyl-p-cresol	Ionol	0.15
Zinc stearate	-	1.54

- A dilute resin solution comprising up to about 50 parts by weight resin, 10 preferably up to about 25 parts by weight resin and more preferably up to about 10 parts by weight resin and a volatile solvent, preferably acetone, is slowly added to the monomer, peroxides and inhibitor in a Ross double planetary mixer and mixed to produce a homogeneous solution. Zinc stearate, a mold release agent, is then added and thoroughly mixed into the solution. The solution is added incrementally to the 15 filler and mixed until all filler is completely dispersed. Another 100 parts by weight of acetone is added and the mixture is mixed for 15 minutes. The resulting particulate material is removed from the mixer and spread on screens and allowed to dry at room temperature. Residual solvent is removed in a drying oven at 120°C. The material is then passed through a coarse screen.

-13-

The material was molded into rectangles about 4.21 inches (107 mm) long, 1.76 inches (44.7 mm) wide and 0.2 inches (5 mm) thick by compression molding at 180°C for four minutes. The rectangles were further cured in an oven at 240°C. The rectangles were checked for shrinkage using ASTM D-955 in the X and Y directions (width and length) and the coefficient of thermal expansion (CTE) was determined at a temperature range from 30°C to 145°C in both the X and Y directions according to 5 ASTM D-696. Shrinkage is reported as linear shrinkage per unit length of the molded composite.

10

Table 4

Ex.	Filler Type	Linear shrinkage per unit length of the molded composite		CTE (micrometers/meter°C)	
		Length	Width	X	Y
9*	84 wt% Asbury A99	0.00653	0.00670	15.0	14.7
10	15 wt% Avcarb Carbon Fiber 69 wt% Asbury 230U	0.00119	0.00187	11.6	9.44
11	30 wt% Avcarb Carbon Fiber 54 wt% Asbury 230U	0.00085	0.00125	3.45	5.32
12	10 wt% Zoltek Panex P33 Carbon Fiber 74 wt% Asbury A99	0.00335	0.00335	10.4	10.3
13	15 wt% Zoltek Panex P33 Carbon Fiber 69 wt% Asbury A99	0.00154	0.00210	9.34	9.6
14	50 wt% Asbury 3621 34 wt% Asbury A99	0.00069	0.00085	4.64	5.58

\*Example 9 is a control example that contains no fiber or platelets.

-14-

Table 5

Ex.	Filler	Flex Stress (psi /Mpa)	Flex Modulus (Kpsi/Mpa)	Thermal Conductivity (W/m °K)	Volume Resistivity (ohm-cm) at 0.125 inch
9*	84 wt% Asbury A99	3821 / 26.35	970 / 6689	16.0	0.0253
10	15 wt% Avcarb Carbon Fiber 69 wt% Asbury 230U	3239 / 27.33	1003 / 6917	9.89	0.0321
11	30 wt% Avcarb Carbon Fiber 54 wt% Asbury 230U	3700 / 25.52	1052 / 7255	7.125	0.0338
12	10 wt% Zoltek Panex P33 Carbon Fiber 74 wt% Asbury A99	2784 / 19.2	627 / 4324	11.46	0.0254
13	15 wt% Zoltek Panex P33 Carbon Fiber 69 wt% Asbury A99	3576 / 24.4	852 / 5876	9.16	0.0276
14	50 wt% Asbury 3621 34 wt% Asbury A99	-	-	10.55	0.026

\*Example 9 contains no fiber or platelets.

5        The comparison of the results of Examples 10-14 with Example 9 demonstrates the value of fibrous and platelet fillers in the composite material. In Examples 10-14 the amount (weight percent based on the total weight of the composite material) of filler is kept constant at 84 wt% while the composition of the filler is varied. In Example 9 Asbury A99 is used exclusively.

10      The conductive moldable composite material as well as articles made from it are economical to produce due to the inexpensive starting materials as well as the use of conventional processing equipment.

-15-

While preferred embodiments have been shown and described, various modifications and substitutions may be made thereto without departing from the spirit and scope of the invention. Accordingly, it is to be understood that the present invention has been described by way of illustration and not limitations.

5           What is claimed is:

-16-

1. A composite material for the manufacture of electrochemical cell components comprising:

a thermosetting resin system and conductive filler wherein the thermosetting resin system comprises a polybutadiene or polyisoprene resin and the composite material has a volume resistivity of about 0.116 ohm-cm or less.

2. The thermosetting resin system of Claim 1 further comprising an unsaturated butadiene- or isoprene-containing polymer, wherein the volume to volume ratio of the polybutadiene or polyisoprene resin to the unsaturated butadiene- or isoprene-containing polymer is between 1:9 and 9:1, inclusive.

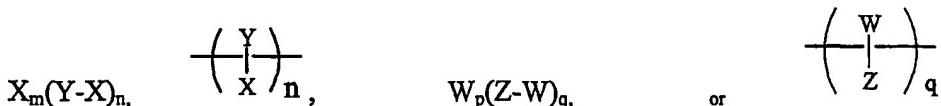
3. The thermosetting resin system of Claim 2 wherein the unsaturated butadiene- or isoprene-containing polymer is a copolymer of isoprene or butadiene and a second monomer.

4. The thermosetting resin system of Claim 3 wherein the unsaturated butadiene- or isoprene-containing polymer is a di-block copolymer.

5. The thermosetting resin system of Claim 4 wherein the unsaturated butadiene- or isoprene-containing polymer is a styrene-butadiene or  $\alpha$ -methyl styrene-butadiene di-block copolymer.

-17-

6. The thermosetting resin system of Claim 3 wherein the unsaturated butadiene- or isoprene-containing polymer is a thermoplastic elastomer block copolymer having one of the formula where in each formula Y is a block comprising isoprene or butadiene units, X is a



thermoplastic block, and m and n represent the average block numbers in said copolymer, m being 0 or 1 and n being at least 1; and Z is a polyethylene or ethylene-propylene copolymer block, W is a thermoplastic block, and p and q represent the average block numbers in said copolymer, p being 0 or 1 and q being at least 1.

7. The composite material of Claim 1 wherein the conductive filler is synthetic graphite.

8. The thermosetting resin system of Claim 1 further comprising a curing agent, preferably dicumyl peroxide, di(2-tert-butylperoxyisopropyl) benzene, t-butylperbenzoate, 2,5-dimethyl-2,5-di(t-butyl peroxy) hexyne-3, and combinations thereof.

9. The thermosetting resin system of Claim 1 wherein the liquid polybutadiene or polyisoprene resin has a molecular weight of less than 5,000, preferably 1,000 to 3,000.

10. The thermosetting resin system of Claim 1 further comprising a functionalized liquid polybutadiene or polyisoprene resin and/or at least one monomer with vinyl unsaturation.

-18-

11. The thermosetting resin system of Claim 16 wherein the at least one monomer with vinyl unsaturation is selected from the group consisting of styrene, vinyl toluene, divinyl benzene, triallylcyanurate, diallylphthalate, and multifunctional acrylate monomers.

12. The composite material of Claim 1, wherein the composite material comprises, based on the total material, about 10 to about 90 volume percent of the conductive filler.

13. The composite material of Claim 1, wherein all or part of the conductive filler is in the form of fibers, platelets, or a combination of fibers and platelets.

14. The composite material of Claim 1, wherein the composite material has a volume resistivity of about 0.08 ohm-cm or less.

15. The composite material of Claim 1, wherein the composite material has a thermal conductivity of at least about 5 watts/meter °K.

16. An article molded from the composite material of Claim 1, wherein the article has a linear shrinkage per unit length of the molded composite in the X-Y plane of less than or equal to about 0.005.

17. A method of making a composite material for the manufacture of electrochemical cell components comprising:

making a dilute solution of a thermosetting resin system comprising polybutadiene or polyisoprene resin in a volatile solvent;  
slowly adding the dilute solution to a conductive filler; and  
mixing to form a homogenous solution.

-19-

18. The method of Claim 17 wherein the thermosetting resin system further comprises an unsaturated butadiene- or isoprene-containing polymer capable of participating in cross-linking with the polybutadiene or polyisoprene resin during cure, and further wherein the volume to volume ratio of the polybutadiene or polyisoprene resin to the unsaturated butadiene- or isoprene-containing polymer is between 1:9 and 9:1, inclusive.

19. The method of Claim 18 wherein the unsaturated butadiene- or isoprene-containing polymer is a copolymer of isoprene or butadiene and a second monomer.

20. The method of Claim 17 wherein the conductive filler is synthetic graphite.

21. A conductive composite material comprising a thermosetting resin system and conductive filler, wherein the thermosetting resin system comprises a polybutadiene or polyisoprene resin, and further wherein the composite material is formed into an electrochemical cell component having a volume resistivity of 0.116 ohm-cm or less.

22. An electrochemical cell component formed from the composition of claim 1.

23. A bipolar plate formed from the composition of claim 1.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
21 February 2002 (21.02.2002)

PCT

(10) International Publication Number  
**WO 02/015302 A3**

- (51) International Patent Classification<sup>7</sup>: H01M 8/02, H01B 1/20
- (81) Designated States (*national*): AB, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.
- (21) International Application Number: PCT/US01/41713
- (22) International Filing Date: 14 August 2001 (14.08.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
60/225,158 14 August 2000 (14.08.2000) US  
60/264,150 25 January 2001 (25.01.2001) US
- (71) Applicant: **WORLD PROPERTIES INC.** [US/US]; Suite 410, 7366 North Lincoln Avenue, Lincolnwood, IL 60646 (US).
- (72) Inventors: FITTS, Bruce, B.; 86 Jacques Road, Danielson, CT 06239 (US). LANDI, Vincent, R.; 240 Green Hollow Road, Danielson, CT 06239 (US). ROY, Saroj, K.; 840 North Main Street, Danielson, CT 06239 (US).
- (74) Agent: REIMER, Leah, M.; Cantor Colburn LLP, 55 Griffin Road South, Bloomfield, CT 06002 (US).

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

(88) Date of publication of the international search report:  
23 January 2003

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



**WO 02/015302 A3**

(54) Title: THERMOSETTING COMPOSITION FOR ELECTROCHEMICAL CELL COMPONENTS AND METHODS OF MAKING THEREOF

(57) Abstract: A conductive, moldable composite material for the manufacture of electrochemical cell components comprising a thermosetting resin system and conductive filler wherein the thermosetting resin composition comprises: (1) a polybutadiene or polyisoprene resin; (2) an optional functionalized liquid polybutadiene or polyisoprene resin; (3) an optional butadiene- or isoprene-containing copolymer; and (4) an optional low molecular weight polymer. In a preferred embodiment, the conductive moldable composite material is used to form a bipolar plate, current collector or other electrochemical cell component. Articles made of the conductive moldable composite material are resistant to chemical attack and hydrolysis, have excellent mechanical strength and toughness, have a volume resistivity of about 1.006 ohm-cm or less and preferably about 0.04 ohm-cm or less and a thermal conductivity of at least about 5 watts/meter °K.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 01/41713

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 H01B1/20 H01M8/02

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01B H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

CHEM ABS Data, WPI Data, PAJ, EPO-Internal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p><b>DATABASE WPI</b>            Section Ch, Week 198730            Derwent Publications Ltd., London, GB;            Class A12, AN 1987-210844            XP002210989            -&amp; JP 62 138549 A (IDEMITSU PETROCHEM CO),            22 June 1987 (1987-06-22)            abstract</p> <p>---</p>	1-7
X	<p><b>DATABASE WPI</b>            Section Ch, Week 198706            Derwent Publications Ltd., London, GB;            Class A85, AN 1987-040175            XP002210990            -&amp; JP 61 296067 A (TOSHIBA CHEM CORP),            26 December 1986 (1986-12-26)            abstract</p> <p>---</p>	1-7

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority, claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*&\* document member of the same patent family

Date of the actual completion of the international search

26 August 2002

Date of mailing of the International search report

10/09/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax: (+31-70) 340-3016

Authorized officer

Riba Vilanova, M

## INTERNATIONAL SEARCH REPORT

ational Application No

PCT/US 01/41713

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 06, 22 September 2000 (2000-09-22) -& JP 2000 077079 A (NIPPON PILLAR PACKING CO LTD), 14 March 2000 (2000-03-14) abstract ----	1-7, 21-23
A	EP 0 297 888 A (LION CORP) 4 January 1989 (1989-01-04) page 3, line 4 - line 61 example 1 table 1 claims ----	1
A	EP 0 109 824 A (MEIDENSHA ELECTRIC MFG CO LTD) 30 May 1984 (1984-05-30) page 1, line 2 -page 3, line 7 ----	1
A	GB 1 264 741 A (SHELL INTERNATIONALE MAATSCHAPPIJ NV) 23 February 1972 (1972-02-23) the whole document -----	3-6

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No  
PCT/US 01/41713

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
JP 62138549	A	22-06-1987	JP JP	1896579 C 6021213 B		23-01-1995 23-03-1994
JP 61296067	A	26-12-1986	JP	5005264 B		21-01-1993
JP 2000077079	A	14-03-2000	JP	3008022 B2		14-02-2000
EP 0297888	A	04-01-1989	JP JP AT DE DE EP US	1011161 A 8013902 B 84901 T 3877635 D1 3877635 T2 0297888 A1 4971726 A		13-01-1989 14-02-1996 15-02-1993 04-03-1993 03-06-1993 04-01-1989 20-11-1990
EP 0109824	A	30-05-1984	JP JP JP JP JP JP AT AT DE DE EP EP US US US	59132504 A 1852370 C 5056627 B 59138067 A 59091135 A 59120641 A 54511 T 63403 T 3381727 D1 3382280 D1 0109824 A1 0190772 A2 4585578 A 4551267 A 4562113 A		30-07-1984 21-06-1994 20-08-1993 08-08-1984 25-05-1984 12-07-1984 15-07-1990 15-05-1991 16-08-1990 13-06-1991 30-05-1984 13-08-1986 29-04-1986 05-11-1985 31-12-1985
GB 1264741	A	23-02-1972	BE DE FR NL	747591 A2 2015249 A1 2042247 A5 7004513 A		21-09-1970 08-10-1970 05-02-1971 05-10-1970